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Keywords
Grinding, Solid-state NMR, Characterization, Waste management

Disciplines
Environmental Sciences | Process Control and Systems

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Abstract

Concrete grinding from highway maintenance operations produces large amounts of a highly basic liquid residue, posing a significant challenge to proper disposal. To discard this residue with little risk to human health or the environment, it should be solidified and its pH should be neutralized. Herein we present the serendipitous discovery that both goals can be met by treatment with citric acid. Through the use of ^{13}C and ^{29}Si solid-state NMR we determined that such treatment removes the calcium from the concrete structure, thus allowing the solubilization of its one-dimensional silica chains. These silica chains then cross-link in solution forming a highly porous silica material that is able to absorb the water from the residue. This new waste treatment process, which may utilize other acids with low water content, promises to facilitate a significantly improved methodology for the disposal of concrete grinding residue in a safe and environmentally friendly manner.

1. Introduction

Roadways are among the most important pieces of infrastructure in the world today. In the U.S. alone, there are approximately 6.5 million kilometers of roadways, with the interstate system by itself consisting of over 73,000 km of highways.[1] Modern roadways are built from either asphalt or concrete, with the choice between the two materials dictated by a variety of factors. Generally, concrete is more expensive than asphalt but lasts longer if properly maintained. One of the maintenance techniques for concrete highways is diamond concrete grinding and grooving, which is widely used to improve ride quality and extend roadway life.[2] Grinding consists of removing 5-7 mm of the surface to yield a level, smooth, and quieter riding surface, whereas grooving consists of cutting into the concrete surface. The resulting channels reduce hydroplaning and potential accidents by providing an escape path for water.[3] These techniques are indispensable, given that the surface quality of roadways, especially highways, has a significant impact on vehicle safety, ride quality, and noise emission.[4] The lifespan of a diamond ground concrete roadway surface is approximately 14 years, which means that a maintenance cycle of 8 to 15 years is typically required.[5]

The diamond grinding process utilizes diamond-impregnated grinding wheels that range from 0.9-1.2 m in width.[2] Water is used in the process to cool the grinding wheel, decrease dust generation, and facilitate removal of the concrete grinding residue (CGR). CGR cannot be allowed to simply flow from the road surface to the adjacent environment, and is typically picked up by a vacuum truck, or sweeper truck, which follows the grinding equipment.[6] Treatment of

CGR varies depending on the jurisdiction and its chemical characteristics. Disposal methods include: spreading, collection and pond decanting, collection and plant processing, collection and recycling, and further alternative methods.

Due to the high pH (pH = 12.1-12.5 in our samples) of the CGR, spreading of this material on land is potentially problematic and prohibited in many jurisdictions. In cases where disposal of CGR by spreading is deemed acceptable, proper engineering controls must be put in place to ensure that the CGR does not enter any sensitive areas. Although there are studies that indicate no negative impact of land spreading CGR,[7] there may be regulatory policies that prohibit disposal of high pH material on land. A second issue which complicates the disposal of raw CGR is that it is in a slurry state, and regulations are far stricter for liquids than they are for solids. In cases where land spreading of CGR is not allowed, a common practice is to store the CGR in bins, or lined pits, to allow the material to dewater. This water is then either treated and discharged[6] or re-used in the grinding process. The remaining sludge may be left in the bins/pits to be naturally dried. This process takes a very long time and requires a large footprint. Alternatively, additional materials may be added, such as various polymers or bulking agents, to solidify this sludge so it may be disposed of as a solid in a shorter timeframe.

Clearly, a solidification solution that also simultaneously reduces the pH to acceptable levels would drastically simplify the disposal of CGR waste. Through experimentation, it was discovered that the addition of citric acid to the raw CGR, in order to neutralise the pH, resulted in a spontaneous solidification of the waste product within hours, in addition to the neutralization

of the pH (see Figure 1). The exact timing for the solidification reaction was dependent on the citric acid dosage. This highly surprising, and potentially useful, reaction is, to the best of our knowledge, undocumented. We have thus sought to employ solid-state nuclear magnetic resonance (SSNMR) spectroscopy, powder X-ray diffraction (PXRD), and N_2 sorption measurements in order to determine the identity of the solid product as well as the mechanism of the solidification reaction. For brevity, this solid product shall be referred to CGRC (CGR citrate). By gaining a thorough chemical understanding of this process, its potential impacts to the concrete grinding industry will be assessed.

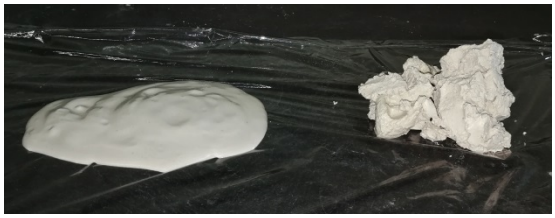

Figure 1. A sample of CGR is depicted on the left with the result of a treatment with citric acid shown on the right demonstrating the solidification of the waste product.

2. Materials and Methods

2.1 Materials

The raw CGR was obtained from the grinding operations of a highway maintenance project during August of 2017 in Ontario, Canada. Anhydrous food grade citric acid was manufactured by TTCA in Shandong, China and calcium citrate tetrahydrate was obtained from Aldrich. The solids content of the CGR varied depending on a number of factors, such as weather, amount of concrete to be ground off, concrete roadway composition, operator preferences, etc. Generally, it was found that for the CGR solidification to be successful, both the liquid and solid constituents

are required, with solids representing a minimum of 30%. In a typical case, with 43% solids, 6% w/w of citric acid needed to be added in order to fully solidify the CGR. Importantly, if the reaction is left to proceed in the absence of stirring, a discreet solid product (CGRC) will form within the liquid phase as a 'crust' on the top surface of the CGR. This thus implies that, upon reacting, a portion of the CGR solid is solubilized such that it may react in the liquid phase; it is the resulting solid that was analyzed in this work.

For the sorption studies, *vide infra*, additional treatments of these materials were required. In the case of the raw CGR, 1 mL was mixed with deionized water (11 mL, 17.4 MΩ). The reaction mixture was continuously shaken at 200 rpm for 15 h. The mixture was then centrifuged at 8000 rpm for 10 min and washed three times with 15 mL of water. The sample was dried in an oven at 70 °C overnight.

Removal of calcium citrate from CGRC was performed by dissolution with HCl. In this case, 2 g of CGRC was mixed with deionized water (40 g, 17.4 MΩ) after which 12 mL of concentrated HCl was slowly added to the sample. The mixture was then continuously stirred at 300 rpm for 15 h. Subsequently, the reaction mixture was centrifuged at 8000 rpm for 10 min and washed three times with 40 mL of water. The sample was then dried in an oven at 70 °C overnight.

2.2 Solid-State NMR Spectroscopy

All SSNMR experiments were performed using an Agilent Technologies DD2 spectrometer operated at a field of 9.4 T (ν_0 = 399.99 MHz for ^{1}H, 100.58 MHz for ^{13}C, and 79.46 MHz for ^{29}Si). The experiments used a 5-mm magic angle spinning (MAS) probe manufactured by Chemagnetics. Samples were packed into 5-mm pencil-type zirconia rotors and spun at 8 kHz for all measurements. The ^{13}C SSNMR spectra of pure citric acid and calcium citrate tetrahydrate were acquired using cross-polarization (CPMAS), with the contact time set to 5 ms and the ^{1}H excitation pulse set to 5 μs. A total of 512 scans were accumulated, with the recycling delay set to 4 s for calcium citrate tetrahydrate and 30 s for citric acid. In the case of the CGRC material, CPMAS was found to be ineffective, perhaps due to the presence of paramagnetic iron, and thus a simple Bloch decay experiment was used; here referred to simply as ^{13}C MAS. The ^{13}C excitation pulse lasted 5 μs and a total of 8192 scans were accumulated with a 6 s recycling delay. ^{29}Si MAS spectra of the CGR and CGRC materials were acquired with the ^{29}Si excitation pulse lasting 5 μs and the recycling delay set to 60 s. A total of 3798 scans were accumulated for CGR while 1750 scans were accumulated for the CGRC material.

2.3 Nitrogen Sorption Studies

Nitrogen sorption isotherms were measured at -196 °C using a Micromeritics ASAP 3000 analyzer. The Brunauer-Emmett-Tell (BET) model[8] was used to calculate the specific surface area. The pore volume was calculated by the Barrett-Joyner-Halenda (BJH) method.[9] Sample pre-treatment for textural property measurements was done by flowing N_2 for 6 h at 100 ºC. For the CGRC sample which was treated with HCl, surface area measurements were performed using a Micromeritics ASAP 2020 system with a pre-treatment of flowing N_2 for 6 h at 160 °C. Pore

size and pore volume were calculated using the nonlocal density functional theory (NLDFT) method.[10,11]

2.4 Powder X-Ray Diffraction

Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker X–ray diffractometer using Cu Kα radiation (40 kV, 44 mA) over a 2θ range of 10–100°. The PXRD patterns were indexed to the structures of dolomite (JCPDS 00-036-0426), calcite (JCPDS 00-005-0586), quartz (JCPDS 00-046-1045), and, in the case of the sulfuric acid-treated sample, bassanite (JCPDS 00-041-0224).

3. Results and Discussion

Concrete is composed principally of cement, water, and aggregates such as limestone and granite. To prepare concrete, these ingredients are mixed in slurry state, which subsequently hardens and solidifies through the dissolution of the silicate monomers (Q^0, where in Q^n, n indicates the number of Si-O-Si links associated with a given site) of tricalcium silicate (Ca_3SiO_5), which then react with each other forming one-dimensional silica chains held together by calcium ions.[12,13,14,15,16,17] As can be seen in Figure 2, the ^{29}Si MAS spectrum of CGR is dominated by Q^2 silicon sites, whereas Q^1 silicon sites situated at the ends of the silica chains were mostly consumed as the silica chains grew. Note that we observe a much higher fraction of Q^2 silicon than was found in academic studies of cement hydration, which reported significant concentrations of Q^1 silicon.[12,13,14,15,16,17,18,19,20] Our lower Q^1 content, indicative of longer chains, is likely the result of carbonation as the sample had been exposed to air for a

prolonged period of time.[21,22] Aside from leading to longer silica chains, carbonation also can lead to cross-linking between chains and the formation of Q^3 silica sites; some intensity near -90 ppm may be caused by such cross-linking. Smaller Q^0 and Q^4 signals are also detected, which correspond to unreacted monomers, as well as quartz, which was found to be present in this material using PXRD measurements. PXRD also revealed the presence of significant amounts of calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) which are likely from the aggregates in the concrete but may also have been formed as a result of carbonation (see Figure 3).

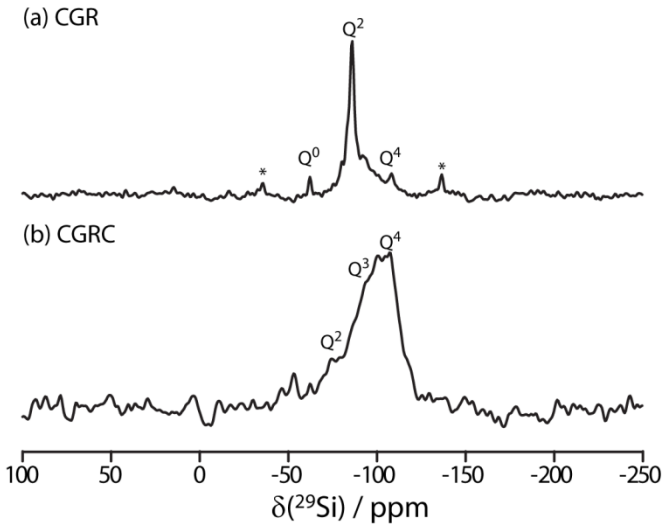

Figure 2. ^{29}Si MAS spectra of CGR (a) and the CGRC product (b).

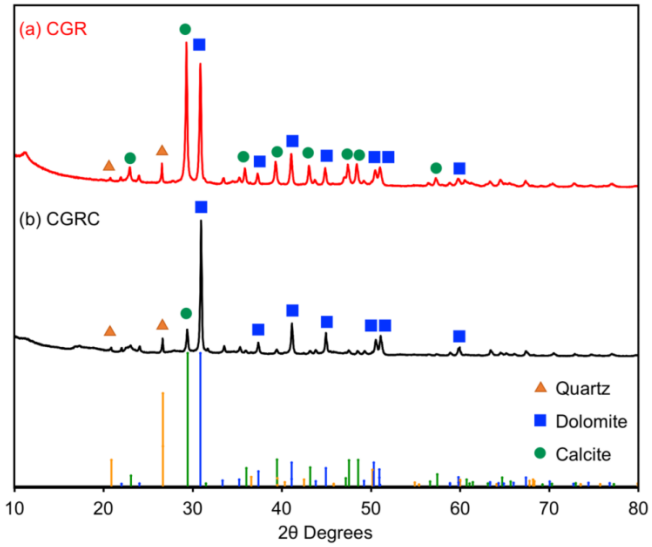

Figure 3. PXRD patterns of (a) CGR and (b) CGRC. Reflections of quartz, dolomite and calcite are identified by triangles, squares and circles, and provided as a reference at the bottom, in orange, blue and green, respectively.

Next, we studied the CGRC material which formed as an isolatable solid product during the reaction of CGR and citric acid. The ^{13}C MAS spectrum of CGRC (see Figure 4c) features resonances that can be assigned to various carbon sites in citrate (*vide infra*) as well as carbonate from the calcite and dolomite phases detected by PXRD (Figure 3). Importantly, while the diffraction pattern of CGRC reveals the same crystalline phases as those present in CGR, a dramatic loss of the intensity of calcite is evident suggesting that the treatment with citric acid has largely dissolved this phase. In order to determine the identity of the citrate in the CGRC material we have additionally acquired the ^{13}C CPMAS spectra of pure citric acid and calcium citrate tetrahydrate shown in Figure 4a and b. The ^{13}C resonances from the CGRC material align perfectly with those of calcium citrate tetrahydrate but are further broadened by the presence of paramagnetic impurities. The resonance from the CH_2 sites (δ = 48 ppm) in particular, which had

the broadest resonance in the crystalline sample, was broadened beyond detection. The paramagnetic impurities additionally reduced $T_{1\rho}$ for both ^{13}C and ^{29}Si such that cross-polarization was ineffective. This data thus demonstrates that the citric acid removes the calcium from the concrete to form a calcium citrate phase which is similar to the crystalline tetrahydrate form. Note that this calcium citrate does not appear to diffract and thus it is likely that is forms a thin layer around the silica particles (*vide infra*), similarly to what was observed recently in the case of sodium citrate at the surfaces of gold nanoparticles.[23] The fate of concrete's 1D silica chains following the removal of the calcium ions can be determined from the ^{29}Si MAS spectrum. As can be seen in Figure 2b, the chemical identity of the CGRC material has diverged significantly from that of the parent CGR and is now mainly composed of Q^4 and Q^3 silicon sites, indicative of the formation of a three-dimensional silica material.[24,25,26]

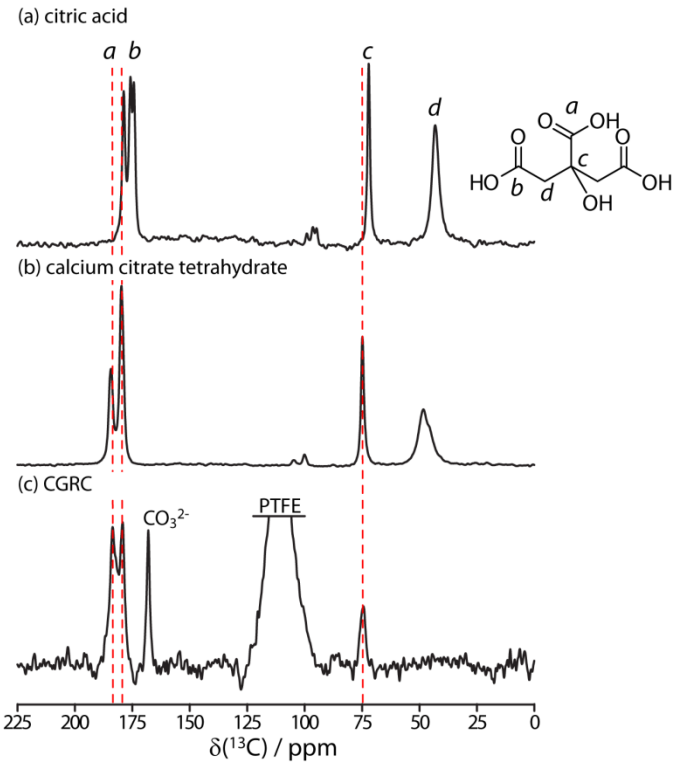

Figure 4. ^{13}C CPMAS spectra of citric acid (a) and calcium citrate tetrahydrate (b), as well as the Bloch decay MAS spectrum of the CGRC product (c). Dashed red lines are added to mark the positions of the resonances belonging to calcium citrate tetrahydrate. Additional resonances are observed in (c) from carbonate (CO_3^{2-}) and the PTFE cap from the MAS rotor. The resonances from the citric acid molecule are assigned (*a*-*d*) to the structure in (a).

Taken together, the SSNMR and PXRD data are used to elucidate the mechanism responsible for the formation of the CGRC solid (Figure 5). Namely, citric acid firstly protonates the silica chains found in the calcium silicate hydrate phase of concrete and complexes with their Ca^{2+} ions. This reaction effectively removes the "glue" which holds these silica chains together; these are solubilized and enter the liquid phase of CGR. Note that this solubilization is known to occur given that CGRC forms as a solid product within the liquid phase which is spatially distinct from the remaining CGR solids. Analogously to the hydration of cement, these polymeric chains then cross-link and precipitate as amorphous silica. We then hypothesize that this silica is reasonably porous such that it can absorb the bulk of the water from the CGR leading to its solidification.

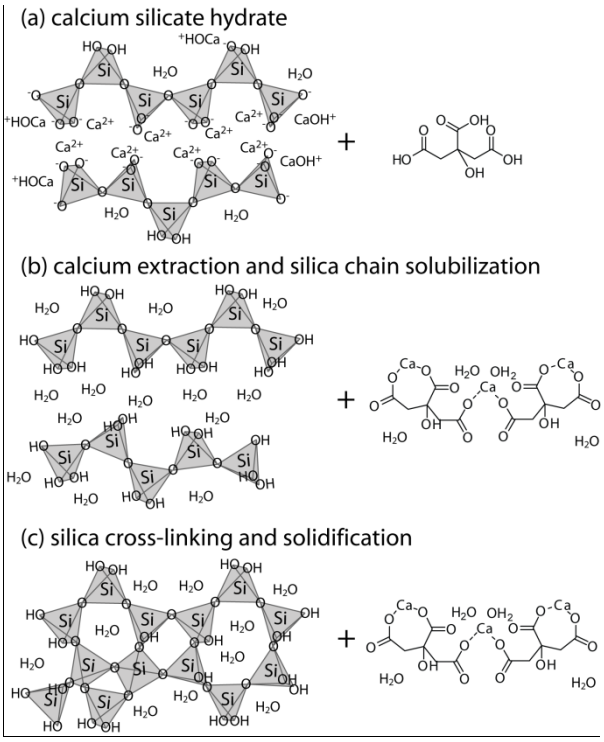

Figure 5. The structure of the calcium silicate hydrate phase of concrete, which consists of 1D silica chains held together by Ca^{2+} ions, is depicted in (a). The molecular structure of citric acid is also shown. The result of a treatment of concrete with citric acid is shown in (b). The calcium is extracted from the structure to form calcium citrate tetrahydrate. This reaction then enables the solubilization of concrete's silica chains. The chains cross-link in solution to form a porous silica framework which traps water, thus leading to the solidification of the CGR (c).

Finally, to test our assumption that the silica produced is capable of absorbing the necessary amounts of water, we performed nitrogen sorption studies of the CGR and CGRC materials (see Figure 6). As could be expected, the raw concrete residue had a relatively low surface area and pore volume of 42.1 m^2/g and 0.14 cm^3/g, respectively. This result was also replicated in the raw CGRC material, see Table 1. This can be understood given that the CGRC material contains both silica as well as calcium citrate tetrahydrate. We have thus additionally treated the CGRC

material with HCl to remove the calcium citrate and analyze solely the silica material. This treatment also removed some carbonates which were present in the CGRC, *vide supra*. Following this treatment, the measured surface area increased to 253 m^2/g and the pore volume increased to 0.43 cm^3/g. We were additionally able to determine the pore size distribution of this material which averaged 1.1 nm. This is slightly larger than the typical pore diameters found in zeolites whose properties as desiccants are widely known. Importantly, treating the raw concrete with HCl did not lead to any increase in porosity, thus providing further support that the greatly enhanced porosity of the CGRC material is responsible for the solidification of CGR when it is treated with citric acid.

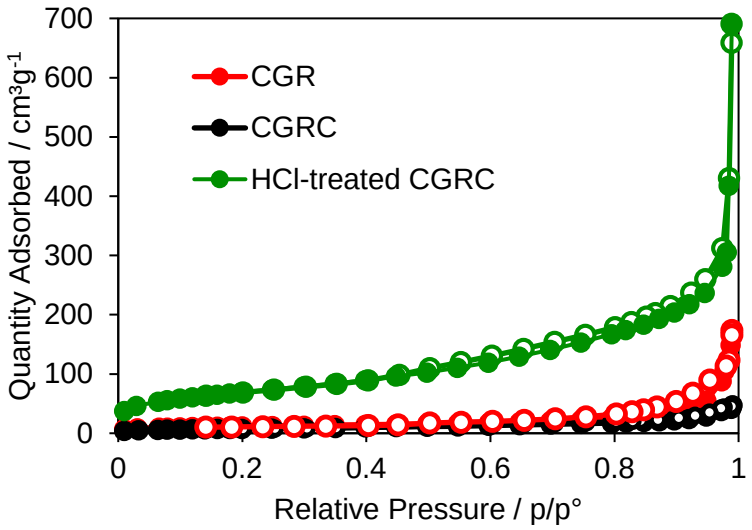

Figure 6. Nitrogen physisorption isotherms of CGR, CGRC and CGRC washed with HCl to remove the calcium citrate.

Table 1. Surface properties of concrete samples after different treatments

Material[a]	Surface Area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore size (nm)
CGR	42.1	0.14	-

HCl-treated CGR	74.5	0.11	-
CGRC	27.7	0.058	-
HCl-treated CGRC	253	0.43	1.1

[a]All samples were washed with water before any additional treatments and were dried prior to the measurements, see section 2.1.

Encouraged by these results, we set out to determine whether analogous reactions would also take place when treating CGR with other acids. In all cases, aqueous solutions of common acids, such as HCl and acetic acid, failed to lead to the solidification of CGR. This result was likely caused by the acids' relatively high water content which increases the required porosity of the silica material for complete solidification. Concentrated sulfuric acid, however, which has a water content below 3%, did lead to the solidification of the CGR. PXRD was able to show that the main crystalline product of the reaction was bassanite ($Ca(SO4)\cdot 0.5H2O$) and that the reaction indeed proceeded analogously to what was observed when using citric acid (see Figure 7).

It is important to note that this reaction is known to occur in bulk concrete and is responsible for the slow degradation of the material and the eventual conversion of the calcium silicate hydrates to silica gel.[27] The impacts of this reaction regarding the solidification of concrete waste have, however, gone unrecognized. One important distinction in this regard relates to the rate of the reactions. While the degradation of concrete progresses slowly over years, the very same reaction can take place in CGR in a matter of minutes due to its greatly increased surface area. The unique solid-liquid mixture of CGR also enables liquid-phase reactions to take place to form a higher surface-area silica material capable of absorbing the necessary amounts of water for complete waste solidification.

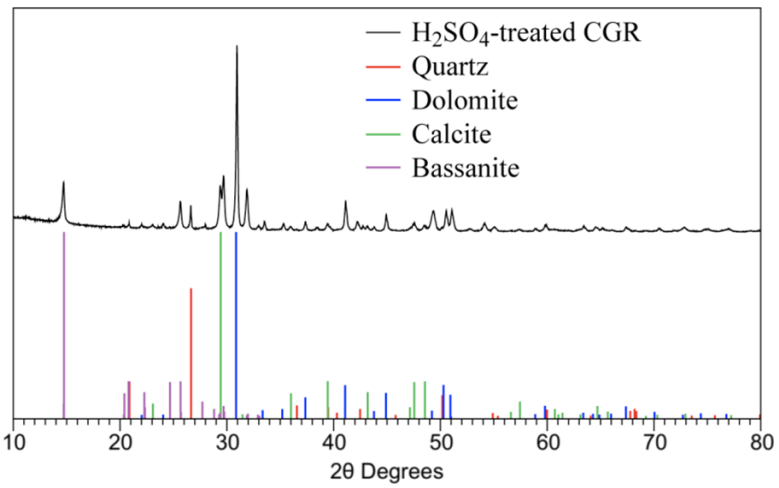

Figure 7. Wide angle PXRD pattern of CGR that was reacted with concentrated sulfuric acid (in a 10:1 weight ratio). The PXRD pattern shows the appearance of bassanite, proving that the reaction proceeds analogously when other acids are used.

4. Conclusions

The reaction of citric acid, and other acids with low water contents, with concrete grinding residue results in a spontaneous solidification of the liquid waste product. By studying the ^{13}C and ^{29}Si SSNMR spectra, as well as the PXRD patterns of the concrete grinding residue and the solidification product, it was determined that the citric acid treatment leads to the extraction of the calcium from the concrete framework. This in turn enables the solubilization of the 1D silica chains found in concrete, which then react to form a microporous silica framework capable of absorbing water from the grinding process. This treatment approach has the potential to enable large scale, simultaneous, solidification and neutralization of concrete grinding residue; greatly simplifying its disposal.

That being said, concrete grinding residue is a waste stream that has a large variation in its characteristics, the most important variable being the solids content. Based on the samples used in this study, it was seen that when the solids content was lower than 30%, solidification does not take place regardless of how much citric acid is added. As such, standard citric acid dosage rate cannot be prescribed since the dosage will depend on the solids content of the waste stream. This also means that this reaction may be economically beneficial in some cases (i.e. when transportation/disposal of liquid is expensive or solids content is high) and ineffective in others (i.e. when there is a liquid waste disposal site close by or solids content is low). Other acids with very low water content, such as concentrated sulfuric acid, were also seen to lead to the spontaneous solidification of concrete grinding residue; however, few can match the low cost and ease of handling of citric acid.

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